Phenylisocyanide Ligand Synthesis and Coordination to Cobalt as a Catalyst for Dimerization of Linear Alpha Olefins

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Linear alpha olefins (LAOs) are used as precursors to various shampoos, lubricants, and detergents, and are essential within the petrochemical industry.[1] This project aims to develop a cationic cobalt catalyst for the linear dimerization of LAOs. The current catalyst yields an unfavorable branched to linear product ratio, which is due to the steric bulk of the supporting ligand.[2] To optimize the formation of the linear product, I synthesized a less bulky supporting ligand using 4-substituted phenylisocyanides. These ligands were successfully coordinated to the neutral pre-catalyst, and various purification techniques were used to isolate the mono-coordinated product required for the dimerization of LAOs.

The current catalyst for the selective dimerization of LAOs uses a phosphite ligand that yields an unfavorable branched to linear product ratio. The sigma bonding of the alkene to cobalt allows for free bond rotation and, due to the size of the supporting ligand, the equilibrium favors C-C bond formation at the less sterically hindered position of the olefin, which gives the branched product via 1,2-insertion. To improve the branched to linear product ratio, we hypothesized that a smaller supporting ligand, with similar electronic properties, could be used, which would favor the desired 2,1-insertion by limiting the steric interaction between the ligand and the alkyl portion of the olefin.

Phenylisocyanides were chosen as the new ligand because they mimic the steric properties of the phosphite ligand but have less steric bulk. The steric bulk is measured in cone angle. By using the phenylisocyanide, the cone is elongated which decreases its angle. This decreases the steric hindrance of the ligand and allows for 2,1-insertion.[3] The goal of this project is to synthesize various 4-substituted phenylisocyanides and coordinate them to $Cp*Co(C_2H_4)_2$ (*aka* bis-ethene), and then activate these compounds with $HBAr^F$ in the presence of linear alpha olefins. This process requires four steps: the synthesis and purification of 4-substituted phenylisocyanides starting with 4-substituted anilines, the synthesis and purification of $Cp*Co(C_2H_4)_2$, the mono-coordination of $Cp*Co(C_2H_4)_2$ with the isocyanide ligands, and the activation of the mono-coordinated product with $HBAr^F$ in the presence of LAOs.

I have successfully coordinated 4-bromo, 4-methoxy, and 4-(trifluoromethyl)phenylisocyanides to the cobalt pre-catalyst. The 4-bromophenylisocyanide, to my surprise, was able to be chromatographed on alumina to give the desired mono-coordinated product in 97.5% purity. The reaction conditions for the coordination of 4-methoxyphenylisocyanide have been optimized to yield >90% purity of the mono-coordinated product without further purification. The synthesis of the mono-coordinated 4-(trifluoromethyl)phenylisocyanide proved to be more difficult due to the electron withdrawing capabilities of the trifluoromethyl group, and mono-coordination reactions were unpredictable and irreproducible under a variety of conditions.

In the future, I will isolate all three products for each phenylisonitrile and gather X-ray crystallography data for each. I will also synthesize $HBAr^F$ for the subsequent activation of the various mono-coordinated pre-catalysts in the presence of linear alpha olefins to determine which is the most active and selective dimerization. The results of these dimerization attempts will be analyzed by NMR and GC-MS, with the goal of determining the effect of a less bulky supporting ligand on the branched to linear product ratio. In addition, the effect of the para substituent on the dimerization will be examined to determine if electron withdrawing or donating ability inhibits the formation of the dimerized product.

Percent Yields from Mono-Coordination Attempts after Purification			
	4-methoxy	4-bromo	4-(trifluoromethyl)
% Mono	91%	97.5%	75%
% Bis	9%	2.5%	12%
% Dimer	0%	0%	13%

Table 1. Percent yields of the three possible products from coordination reactions after reaction optimization and purification.

References:

[1] Lappin, G. R., *Alpha Olefins Applications Handbook*. Marcel Dekker: New York, 1989.

[2] Broene, R. D.; Brookhart, M.; Lamanna, W. M.; Volpe, A. F., Cobalt-Catalyzed Dimerization of α-Olefins to Give Linear α- Olefin Products. *Journal of the American Chemical Society* 2005, *127* (49), 17194-17195.

[3] Morris, J. Phenylisocyanide Ligand Synthesis and Coordination to a Cobalt Catalyst for Dimerization of Linear Alpha Olefins. Bowdoin College, Brunswick, ME, 2019.